

We Claim:

1. An adduct comprising a carbon nanotube and a transitional metal coordination complex, wherein the metal of the complex is attached by a covalent linkage to at least one oxygen moiety on the nanotube.

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2. An adduct as in Claim 1 wherein said covalent linkage is a coordinative linkage.

3. An adduct as in Claim 1 wherein said at least one oxygen moiety is selected from the group consisting of a carboxyl group, a hydroxyl group, an aldehyde group and a ketone group.

4. An adduct as in Claim 1 wherein the transitional metal coordination complex is selected from the group consisting of Wilkinson's complex, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Cr}(\text{ethylenediamine})_3]^{3+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Ni}(\text{C}_5\text{H}_5)_2$, $[\text{PdCl}_4]^{2-}$, $\text{Cr}(\text{CO})_6$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{CoF}_6]^{3-}$, $[\text{Pt}(\text{ethylenediamine})_2\text{Cl}_2]\text{Br}_2$, $[\text{Co}(\text{NH}_3)_4(\text{SCN})\text{Br}]\text{Cl}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CeCl}_6]^{2-}$, $[\text{La}(\text{acetylacetonate})_3(\text{H}_2\text{O})_2]$, $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Er}(\text{NCS})_6]$, $[\text{Lu}(\text{2,6-dimethylphenyl})_4]^-$ and $[\text{Ho}(\text{tropolonate})_4]^-$.

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5. An adduct as in Claim 1 wherein said transitional metal is in the form of a nitrate, a halide, or a salt.

6. An adduct as in Claim 4 wherein said adduct comprises different types of transitional metal coordination complexes.

7. An adduct as in Claim 1 wherein said adduct has high degree of solubility in organic or aqueous solvents.

8. An adduct as in Claim 7 wherein said organic solvent is selected from the group consisting of dimethylsulfoxide (DMSO), tetrahydrofuran (THF) or dimethylformamide (DMF). methanol, ethanol, 2-propanol, acetone, *o*-dichlorobenzene (ODCB), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate, benzene and dimethylformamide (DMF).

9. An adduct as in Claim 4 wherein the transitional metal coordination complex is a Wilkinson's complex.

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10. An adduct as in Claim 9 wherein said adduct is a hexacoordinate structure.

11. An adduct as in Claim 9 wherein the rhodium of said Wilkinson's complex has an oxidation state of three.

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12. An adduct as in Claim 9 wherein said adduct has a solubility of greater than 250 mg/L in DMSO.

13. An adduct as in Claim 9 wherein said adduct has a solubility of greater than 75 mg/L in THF or DMF.

5 14. An adduct as in Claim 1 wherein said carbon nanotube is a semiconductor.

15. An adduct as in Claim 1 wherein said carbon nanotube is a metal.

10 16. An adduct as in Claim 1 wherein said carbon nanotube is single-walled.

17. An adduct as in Claim 1 wherein said carbon nanotube is multi-walled.

15 18. An adduct as in Claim 16 wherein the diameter of said single-walled carbon nanotube is about 0.7 to about 1.5 nm.

19. An adduct as in Claim 14 wherein the diameter of said multi-walled carbon nanotube is about 3 to about 30 nm.

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20. An adduct as in Claim 1 wherein at least one end of the carbon nanotube is open.

21. A method of producing a plurality of carbon nanotubes with increased solubility, the method comprising:

5 adding a solution comprising a transitional metal coordination complex to a carbon nanotube dispersion to form a resultant dispersion comprising carbon nanotube-metal adducts,

wherein a plurality of carbon nanotubes with increased solubility is formed.

22. A method as in Claim 21 wherein 50-99 wt% of said carbon nanotube-metal adduct dispersion comprises nanotubes.

23. A method as in Claim 21 wherein said transitional metal coordination complex is selected from the group consisting of Wilkinson's complex, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$,
15 $[\text{Cr}(\text{ethylenediamine})_3]^{3+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Ni}(\text{C}_5\text{H}_5)_2$, $[\text{PdCl}_4]^{2-}$, $\text{Cr}(\text{CO})_6$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{CoF}_6]^{3-}$, $[\text{Pt}(\text{ethylenediamine})_2\text{Cl}_2]\text{Br}_2$, or $[\text{Co}(\text{NH}_3)_4(\text{SCN})\text{Br}]\text{Cl}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CeCl}_6]^{2-}$, $[\text{La}(\text{acetylacetonate})_3(\text{H}_2\text{O})_2]$, $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Er}(\text{NCS})_6]$, $[\text{Lu}(2,6\text{-dimethylphenyl})_4]^-$, and $[\text{Ho}(\text{tropolonate})_4]^-$.

20 24. A method as in Claim 23 wherein a transitional metal is in the form of a nitrate, a halide, or a salt.

25. A method as in Claim 23 wherein the solution comprises a mixture of different transitional metal coordination complexes.

26. A method as in Claim 21 wherein the nanotube dispersion comprises nanotubes in DMSO, THF or DMF.

5 27. A method as in Claim 21 further comprising precipitating the adduct from the solution.

28. A method of catalyzing a reaction of an unsaturated hydrocarbon comprising:

10 providing a catalyst system comprising a carbon nanotube-transitional metal coordination complex adduct in an organic solvent; and

contacting a reactant and an unsaturated hydrocarbon with said catalyst system,

whereby a reaction of the unsaturated hydrocarbon and the reactant is catalyzed.

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29. A method as in Claim 28 wherein said reaction is selected from the group consisting of a hydrogenation, a hydroformylation, an epoxidation, an olefin metathesis, a hydrosilylation, and an alkene (Ziegler-Natta) polymerization.

20 30. A method as in Claim 28 wherein said organic solvent is a halogenated organic solvent.

31. A method as in Claim 30 wherein said halogenated organic solvent is CHCl_3 .

32. A method as in Claim 28 wherein said transitional metal coordination
5 complex is selected from the group consisting of Wilkinson's complex, $[\text{Ag}(\text{NH}_3)_2]^+$,
 $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$,
 $[\text{Cr}(\text{ethylenediamine})_3]^{3+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Ni}(\text{C}_5\text{H}_5)_2$, $[\text{PdCl}_4]^{2-}$, $\text{Cr}(\text{CO})_6$,
 $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{CoF}_6]^{3-}$, $[\text{Pt}(\text{ethylenediamine})_2\text{Cl}_2]\text{Br}_2$, or $[\text{Co}(\text{NH}_3)_4(\text{SCN})\text{Br}]\text{Cl}$,
10 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CeCl}_6]^{2-}$, $[\text{La}(\text{acetylacetonate})_3(\text{H}_2\text{O})_2]$, $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Er}(\text{NCS})_6]$,
 $[\text{Lu}(\text{2,6-dimethylphenyl})_4]^-$, and $[\text{Ho}(\text{tropolonate})_4]^-$.

33. A method as in Claim 32 wherein a transitional metal is in the form of
a nitrate, a halide, or a salt.

15 34. A method as in Claim 28 wherein the hydrocarbon is an alkene, an
acetylene, an alkadiene, a cycloolefin, a cycloacetylene, a cycloalkene, an alkyne, a
cyclohexene or an aromatic compound.

35. A method as in Claim 28 further comprising recovering the adduct
20 from the catalyst system.

36. A method as in Claim 28 wherein said transitional metal complex is a
Wilkinson's complex and wherein said reaction is a hydrogenation of an unsaturated
hydrocarbon.

37. A catalyst support comprising a plurality of adducts wherein an adduct comprises a carbon nanotube and a transitional metal coordination complex, wherein the metal of the complex is associated by coordinative attachment to at least one oxygen moiety on the nanotube, and wherein the transitional metal coordination complex is capable of catalyzing a reaction.

38. A method of exfoliating a plurality of carbon nanotube bundles, comprising:

contacting a carbon nanotube dispersion comprising a plurality of nanotube bundles wherein the bundles have an average first diameter with a solution comprising transitional metal coordination complexes, thereby exfoliating the bundles,

wherein the exfoliated bundles have an average second diameter.

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39. A method as in Claim 38 wherein said average second diameter is about 10-80 % of said average first diameter.

40. A method as in Claim 38 wherein said exfoliated bundles are about 15-20 nm in diameter.

41. A method as in Claim 38 wherein said bundles are exfoliated to a single nanotube.

42. A method of providing single carbon nanotubes and carbon nanotube bundles with a selected diameter, comprising:

5 contacting a carbon nanotube dispersion with a solution comprising a transitional metal coordination complex, wherein adducts are formed between single nanotubes and said transitional metal complex, and between carbon nanotube bundles of a selected diameter and said transitional metal complex, wherein the selected diameter is less than about 10 nanometers; and

 precipitating the adducts from the solution,

wherein carbon nanotubes with a selected diameter are provided.

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43. A method of modifying a physical property of a nanotube wherein the method comprises:

 contacting a carbon nanotube with a solution of a transitional metal coordination complex to form a carbon nanotube-transitional metal coordination
15 complex adduct,

wherein a physical property of the carbon nanotube is modified.

44. A method according to Claim 43 wherein the physical property is selected from the group consisting of an electronic property, an electrical property, an
20 electromechanical property, an optical property, a chemical property, a mechanical property, a structural property, a thermal property and a thermoelectric property.

45. A method according to Claim 44 wherein the electrical property is selected from the group consisting of conductance, resistivity, carrier mobility, a transport property, permittivity, and a charge transfer property.

5 46. A method according to Claim 45 wherein the modification of conductance is a tunability in conductance.

47. A method according to Claim 44 wherein the structural property is selected from the group consisting of elasticity and ease of composite formation.

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48. A device comprising an adduct wherein the adduct comprises a carbon nanotube and a transitional metal coordination complex, wherein the metal of the complex is associated by coordinative attachment to at least one oxygen atom on the nanotube, wherein the device is selected from the group consisting of a sensor, a
15 device used in molecular electronics, a solar cell, a device used in optoelectronics, a device used in nanocatalysis, and a scanning probe microscopy tip.

49. An adduct comprising a carbon nanotube and a macrocyclic molecule, wherein a functional group attaches the macrocyclic molecule and the nanotube.

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50. An adduct as in Claim 49 wherein said macrocyclic molecule is selected from the group consisting of a coronand, a corand, a cryptand, a spherand, a cryptaspherand, a hemisspherand, a podand, a cavitand, a carcerand, and derivatives thereof.

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51. An adduct as in Claim 49 wherein the macrocyclic molecule comprises oxygen, nitrogen or sulfur atoms.

52. An adduct as in Claim 50 wherein the macrocyclic molecule forms a
5 cavity which is about 0.5 to 10 Angstroms.

53. An adduct as in Claim 50 wherein the macrocyclic molecule comprises a metal ion is selected from the group consisting of a lithium ion, a potassium ion, a calcium ion, a mercury ion, a zinc ion, a strontium ion, and a magnesium ion.

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54. An adduct as in Claim 49 wherein said macrocyclic molecule and said carbon nanotube are covalently linked.

55. An adduct as in Claim 49 wherein said macrocyclic molecule and said
15 carbon nanotube are ionically linked.

56. An adduct as in Claim 49 further comprising an organic molecule linker between the functional group and the macrocyclic molecule, wherein the linker comprises less than about twenty carbon atoms.

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57. An adduct of Claim 49 wherein the adduct has high degree of solubility in an organic solvent or an aqueous solvent.

58. The adduct of Claim 57 wherein the organic solvent is selected from the group consisting of methanol, ethanol, 2-propanol, acetone, *o*-dichlorobenzene (ODCB), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate, benzene and dimethylformamide (DMF).

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59. An adduct according to Claim 50 wherein the macrocyclic molecule is a crown ether.

60. An adduct according to Claim 59 wherein the crown ether has a cavity
10 size from about 1.7 to 3.0 Angstroms.

61. An adduct according to Claim 59 wherein the ring of the crown ether comprises approximately fifteen to forty-four atoms.

15 62. An adduct according to Claim 61 wherein the crown ether is selected from the group consisting of 12-crown-4, 15-crown-5, 18-crown-6, 27-crown-9, 30-crown-10, and dicyclohexano-18-crown-6.

20 63. An adduct of Claim 49 wherein the carbon nanotube is a semi-conductor.

64. An adduct of Claim 49 wherein the carbon nanotube is a metal.

65. An adduct of Claim 49 wherein the carbon nanotube is single-walled.
66. An adduct of Claim 49 wherein the carbon nanotube is multi-walled.
- 5 67. An adduct of Claim 65 wherein the diameter of the single-walled carbon nanotube is about 0.7 to about 1.5 nm.
68. An adduct of Claim 66 wherein the diameter of the multi-walled carbon nanotube is about 3 to about 30 nm.
- 10 69. A method of producing a plurality of carbon nanotubes with increased solubility, the method comprising:
- providing a plurality of carbon nanotubes in the form of bucky paper; and
- dispersing the bucky paper in a solution comprising a plurality of macrocyclic
- 15 molecules to form a resultant dispersion comprising a plurality of nanotube-macrocyclic molecule adducts,
- wherein a plurality of carbon nanotubes with increased solubility is produced.
- 20 70. The method of Claim 69 wherein said macrocyclic molecule is selected from the group consisting of a coronand, a corand, a cryptand, a spherand, a cryptaspherand, a hemisspherand, a podand, a cavitand, a carcerand, and derivatives thereof.

71. The method of Claim 69 wherein the nanotube has functional groups selected from the group consisting of an amino group, a keto group, an aldehyde group, an ester group, an hydroxyl group, a carboxyl group, and a thiol group.

5 72. The method of Claim 69 wherein the macrocyclic molecule has functional groups selected from the group consisting of an amino group, a keto group, an aldehyde group, an ester group, an hydroxyl group, a carboxyl group, and a thiol group.

10 73. The method of Claim 69 wherein the macrocyclic molecule solution comprises is a mixture of different macrocyclic molecules.

74. The method of Claim 69 further comprising recovering the adducts from the resultant dispersion by filtration.

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75. The method of Claim 69 wherein the macrocyclic molecule is a functionalized crown ether.

20 76. The method of Claim 32 wherein the crown ether is selected from the group consisting of 12-crown-4, 15-crown-5, 18-crown-6, 27-crown-9, 30-crown-10, and dicyclohexano-18-crown-6 and mixtures thereof.

77. A method of exfoliating a plurality of carbon nanotube bundles, comprising:

contacting bucky paper with a solution comprising functionalized macrocyclic molecules, wherein said bucky paper comprises a plurality of nanotube bundles having an average first diameter, thereby exfoliating the bundles, wherein the exfoliated bundles have an average second diameter.

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78. The method of Claim 77 wherein the average second diameter is about 10-80 % of the average first diameter.

79. The method of Claim 35 wherein the exfoliated bundles are about 30 to 10 200 nm in diameter.

80. A method of modifying a physical property of a nanotube wherein the method comprises:

providing a plurality carbon nanotubes in the form of bucky paper; and
15 dispersing the bucky paper in a functionalized crown ether solution to form a resultant dispersion comprising nanotube-crown ether adducts,
wherein a physical property of the carbon nanotube is modified.

81. A method according to Claim 80 wherein the physical property is
20 selected from the group consisting of an electronic property, an electrical property, an electromechanical property, an optical property, a chemical property, a mechanical property, a structural property, a thermal property and a thermoelectric property.

82. A method according to Claim 80 wherein the electrical property is selected from the group consisting of conductance, resistivity, carrier mobility, a transport property, permittivity, and a charge transfer property.

5 83. A method according to Claim 82 wherein the modification of conductance is a tunability in conductance.

84. A method according to Claim 81 wherein the structural property is selected from the group consisting of elasticity and ease of composite formation.

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85. A device comprising an adduct wherein the adduct comprising a carbon nanotube and a functionalized crown ether, wherein a functional group on the crown ether is attached to an oxygen atom on the nanotube, wherein the device is selected from the group consisting of a sensor, a device used in molecular electronics,
15 a solar cell, a device used in optoelectronics, a device used in nanocatalysis, and a scanning probe microscopy tip.